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Muonium as a shallow center in GaN

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A paramagnetic muonium (Mu) state with an extremely small hyperfine parameter was observed for the first time in single-crystalline GaN below 25 K. It has a highly anisotropic hyperfine structure with axial symmetry along the $\langle 0001 \rangle$ direction, suggesting that it is located either at a nitrogen-antibonding or a bond-centered site oriented parallel to the c-axis. Its small ionization energy (≤ 14 meV) and small hyperfine parameter ($\sim 10^{-4}$ times the vacuum value) indicate that muonium in one of its possible sites produces a shallow state, raising the possibility that the analogous hydrogen center could be a source of n-type conductivity in as-grown GaN.

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Since the discovery of methods to produce sufficient p-type conductivity by Mg-doping [1, 2], gallium nitride and related compound semiconductors are being aggressively developed for electronic and optelectronic devices such as blue/green lasers and light-emitting diodes. Unique features such as a wide and direct band gap and high breakdown field make the nitrides ideal for such applications. However, as-grown undoped GaN epitaxial thin films, as well as bulk single crystals, commonly exhibit n-type conductivity with concentrations ranging from 10^{16} to 10^{19} cm^{-3}. Extensive experimental and theoretical studies [3] have been undertaken to understand the origin of this n-type conductivity.

For many years, nitrogen vacancies, which are commonly observed in as-grown GaN, were thought to be a major source of the n-type conductivity [4, 5]. Recent theoretical work [6] challenges this view by showing that the nitrogen vacancies have a high formation energy in n-type GaN; hence their concentration is predicted to be too low to affect the electrical conductivity. Moreover, Hall effect measurements on a GaN sample irradiated by high-energy electrons showed that the donor level of the nitrogen vacancies (64(10) meV) was much deeper than that of the residual donors (18 meV) [7]. Contamination by oxygen or silicon is difficult to avoid during crystal growth and both of these impurities have been proposed as the origin of unintentional n-type behaviour. Silicon is often used as an intentional donor dopant and can provide free electron concentrations of up to $10^{20}\,$cm^{-3}. Very recent magneto-optical studies of hydride-vapor-phase epitaxial GaN show that a candidate other than O or Si impurities can also act as a shallow donor [8].

By contrast, magnesium is currently the only acceptor dopant reliably used to obtain p-type GaN. Even in this case, high hole concentrations were difficult to achieve until it was found that hydrogen reacts with and passivates the Mg acceptors [9], similar to its effect on acceptors in Si. A post-growth anneal at high temperature is required to remove H from the vicinity of the Mg dopants and thereby activate p-type electrical properties.

Motivated by such a crucial role of hydrogen in GaN, extensive μSR (muon spin resonance) studies [10] have been performed to clarify the physical and electronic structure of isolated H centers *via* their muonium analog. The results established the existence of two charged states (Mu$^+$ and Mu$^-$) [11, 12], and level-crossing resonance spectra revealed that Mu$^+$ and Mu$^-$ reside at sites anti-bonding to N and Ga, respectively [13].

In addition, neutral paramagnetic muonium states, i.e. Mu^0, are readily observed in a wide variety of semiconductors. While the dynamical aspects (e.g., diffusion) may be considerably different between Mu and H due to the light mass of Mu ($m_\mu \simeq \frac{1}{9} m_p$), the local electronic structure of Mu is virtually equivalent to that of H after a small correction due to the difference in the reduced mass ($\sim 4\%$). Recently, a novel Mu state having an extremely small hyperfine parameter ($10^{-4} \times A_\mu$) was reported in II-VI compound semiconductors including CdS [14] and ZnO [15, 16, 17], implying that Mu (and hence H) can act as a donor in these materials. No Mu^0 hyperfine spin-precession spectra have previously been reported for GaN, although hyperfine decoupling measurements suggest a short-lived atomic-like neutral [13].

In this Letter we report on the first observation of a paramagnetic muonium spectrum in GaN. The observed Mu^0 state has an extremely small and highly anisotropic hyperfine parameter. The location within the band gap for the [0/+] energy level associated with this Mu state is estimated from the measured activation energy for ther-

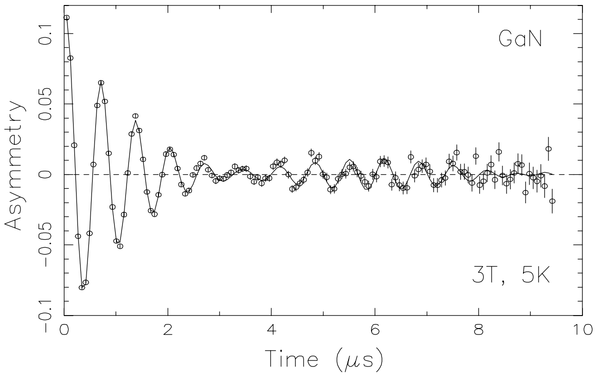

FIG. 1: The μSR time spectrum in GaN at 5.0 K under an external field of 3.0 T applied parallel to the [0001] axis, displayed in a rotating-reference-frame frequency of 405 MHz. A beat pattern due to multiple frequencies is clearly seen.

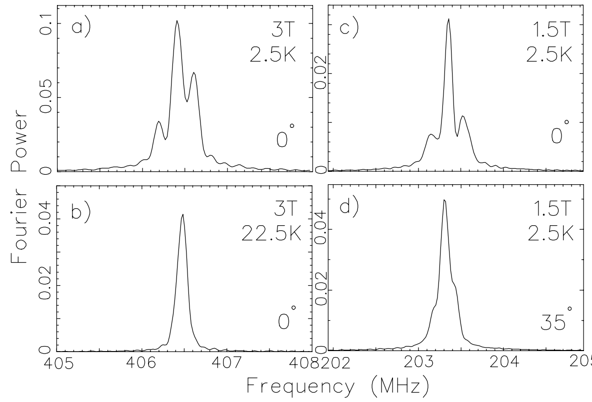

FIG. 2: Frequency spectra obtained for GaN at (a) 2.5 K and (b) 22.5 K with B=3.0 T parallel to [0001] axis, and with B=1.5T at 2.5 K, where [0001] is parallel to B (c) or tilted by 35° from B (d), where from 0.01 μs to 9.60 μs is adopted as a time range of FFT. The number of y-axis in (a) and the other is not directly comparable, because of the difference in the data statistics.

mal ionization. These results imply that an isolated hydrogen impurity would behave as a shallow donor if it were located at the same crystallographic site.

We performed μSR measurements on a GaN single-crystal with the hexagonal (2H) wurtzite structure. GaN has tetrahedral coordination with bonds parallel to the symmetry axis slightly elongated and off-axis bond directions ordered to give hexagonal symmetry around [0001]. The μSR experiment was conducted at the TRIUMF M15 beamline with the Belle spectrometer. Muons from a surface beam (100% spin-polarized with an energy of 4 MeV) with their polarization transverse to the applied magnetic field were implanted into GaN ($3 \times 3 \times 0.5\,\mathrm{mm}$, [0001] orientation, n type with a concentration of $10^{16}\,\mathrm{cm}^{-3}$). The subsequent time evolution of the muon spin precession yields information on the muonium hyperfine parameters and stability of the center. High fields (up to 5 T) were used to quench fast spin relaxation due to interactions with host nuclear spins. The GaN crystal was mounted in a He gas-flow cryostat such that the [0001] and $[11\bar{2}0]$ crystallographic axes could be oriented at specific angles to the applied field in order to examine the symmetry of the hyperfine interaction. Dependences on temperature and magnetic field strength were obtained with the field parallel to the [0001] axis.

Above 25 K, only a single (diamagnetic) precession signal is observed at the muon Larmor frequency (gyromagnetic ratio $\gamma_\mu = 2\pi \times 135.53$ MHz/T). Relaxation of this signal is well described by Gaussian damping with a nearly temperature-independent rate constant of $\simeq 0.2$ $\mu\mathrm{s}^{-1}$. This damping rate is satisfactorily explained by the dipole-dipole interaction of muons with ^{69,71}Ga and ^{14}N nuclei. The muon spin rotation signal changes drastically below 25 K. A typical μSR spectrum is shown in Fig. 1. Fig. 2 shows the angular and temperature dependence of the frequency spectra obtained by Fourier transform, in which one pair of satellite lines is clearly seen with their positions situated symmetrically around the central line, which corresponds to the precession of diamagnetic muons. The splitting of these satellites remained unchanged when the applied field was increased from 1.5 T up to 5 T (see Fig. 2a and 2c), a result that is important in identifying the spectra as due to the hyperfine interaction of a Mu^0 center. The splitting decreases when the [0001] axis is tilted with respect to $\vec{B}$ as in Fig. 2d. Moreover, an equivalent frequency spectrum was observed when the $[11\bar{2}0]$ axis was rotated by 90° around [0001], which was oriented at 35° to the applied magnetic field. These observations demonstrate the presence of a paramagnetic muonium state in GaN. The resulting hyperfine interaction is extremely small, about 10^{-4} times the vacuum value for a Mu atom, and is axially symmetric with respect to [0001].

With the [0001] axial symmetry established qualitatively, a more formal analysis can be undertaken to extract the hyperfine constants. The amplitude differences for the two hyperfine lines allow the specific muonium transition to be assigned to each satellite and establishes the sign of the hyperfine constants. Spin precession signals from the paramagnetic Mu state have two components in the high-field limit ($B \gg 2\pi A/\gamma_e$, where $\gamma_e = 2\pi \times 28.024$ GHz/T is the electron gyromagnetic ratio):

$$\nu_{12}(\theta) \simeq \nu_0 - \frac{1}{2}\Delta\nu(\theta), \quad (1)$$

$$\nu_{34}(\theta) \simeq \nu_0 + \frac{1}{2}\Delta\nu(\theta), \quad (2)$$

$$\Delta\nu(\theta) = A(\theta) = A_\parallel \cos^2\theta + A_\perp \sin^2\theta, \quad (3)$$

where $2\pi\nu_0 = \gamma_\mu B$, θ is the angle between $\vec{B}$ and the [0001] symmetry axis, and $A_\parallel$ and $A_\perp$ are the hyperfine parameters parallel and perpendicular to [0001], respec-

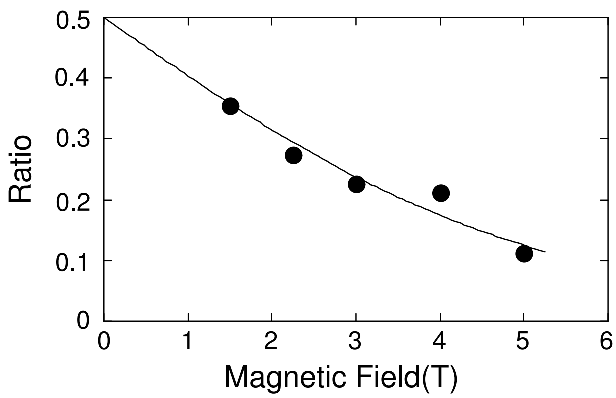

FIG. 3: Magnetic field dependence of the ratio of the lower-frequency satellite amplitudes to the sum of both satellites at 2.5 K (symbols). Solid curve is a fitting result using the Maxwell-Boltzmann distribution with the Mu temperature as a free parameter.

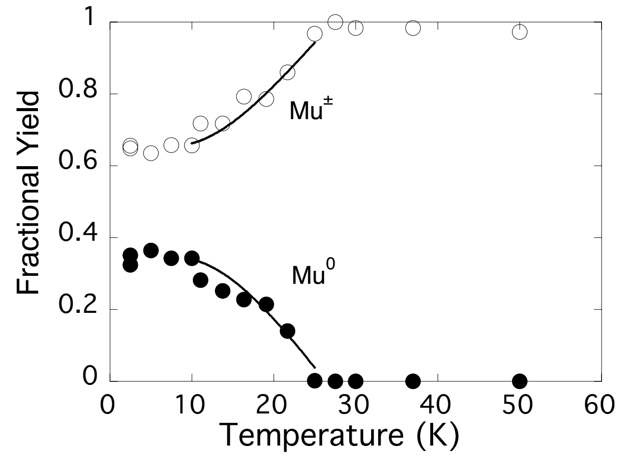

FIG. 4: The fractional yield of Mu (closed circles), and a diamagnetic state (open circles) versus temperature in GaN. Solid curves are fitting results (see text).

tively. The frequencies ν_{12} and ν_{34} correspond to the transitions of spin states between $|s_e, s_\mu\rangle = |+\frac{1}{2}, +\frac{1}{2}\rangle$ and $|+\frac{1}{2}, -\frac{1}{2}\rangle$, and between $|-\frac{1}{2}, +\frac{1}{2}\rangle$ and $|-\frac{1}{2}, -\frac{1}{2}\rangle$, respectively.

Because the population of the $s_e = -\frac{1}{2}$ state is always larger in an applied field, the observations in Fig. 2 imply that the low-frequency line corresponds to $s_e = +\frac{1}{2}$, thus to ν_{12}, and that $A(\theta)$ is positive for the displayed orientations. Results from direct fits to the time-domain spectra (see Fig. 1), where 0.01 μs to 9.60 μs in time range, provide a better amplitude measurement for comparison with theoretical expectations. Analysis assuming three frequency components (ν_0, ν_{12}, and ν_{34}, we assumed the depolarization rates of the two Mu lines are equal) is quite satisfactory, with a reasonably small reduced χ^2 ($\simeq$ 1.55) for the data in Fig. 1. Fig. 3 shows the field dependence for the ratio of the lower-frequency satellite amplitudes to the sum of both satellites at 2.5 K and $\theta = 0$, together with a fitting result of electron spin occupation probabilities for an isolated muonium center unsing the Maxwell-Boltzmann distribution, where 3.4 K was obtained as the Mu temperature. Correspondence between the sample and obtained Mu temperature is also satisfactory, confirming assignment of a positive $A_\parallel$ hyperfine constant.

From the spectrum in Fig. 2a, with $\vec{B}$ applied along [0001], the hyperfine constant is deduced to be

$$A(0^\circ) \;=\; A_\parallel = +337(10)\,\text{kHz}. \quad (4)$$

Combining this result with the data for a tilted sample orientation with respect to $\vec{B}$ (Fig. 2, where $\theta = 35.0^\circ$, and $\Delta\nu = 146(3)$kHz) the remaining hyperfine constant is found to be

$$A_\perp \;=\; -243(30)\,\text{kHz}. \quad (5)$$

As an experimental check, these parameters reproduce the observed splitting for an additional orientation with $\theta = 15.0^\circ$. Therefore, we conclude that the hyperfine parameters parallel and perpendicular to the [0001] symmetry axis have opposite signs. The static dielectric constants in GaN are 10.4 parallel and 9.5 perpendicular to [0001] [3]. Since the degree of anisotropy in the hyperfine tensor for the observed paramagnetic muonium state is much larger than that implied by the dielectric constant, we conclude that the observed anisotropy is due to local site symmetry. Of the likely locations for Mu in the GaN wurtzite structure [18, 19, 20], these results strongly suggest that the paramagnetic Mu center resides at either the $\text{AB}_{N\parallel}$ or the $\text{BC}_\parallel$ site.

The temperature dependence of the amplitudes of the Mu^0 and diamagnetic signals are plotted in Fig. 4. The total amplitude is almost independent of temperature, suggesting that Mu is ionized to a diamagnetic state above 25 K. It seems unlikely that the energy levels are just above the valence band since, if that were correct, Mu should remain neutral due to the bulk n-type conductivity of the present specimen which puts the Fermi level much higher than mid-gap. These results indicate that the observed paramagnetic Mu center acts as a shallow donor. Thus, since Mu centers simulate the electronic structure of H in GaN, our result provides convincing evidence that hydrogen centers at this particular site are shallow donors, and thus would contribute to n-type conductivity in GaN.

The activation energy E_a for Mu ionization was found to be 4.6(6) meV by fitting the data in Fig. 4 over a region from 10 K to 25 K with a function $\alpha + \beta\exp(-E_a/k_BT)$. Interpretation of this energy depends on the precise process forming the neutral charge-state of the Mu donor and the extent to which equilibrium arguments apply to muonium state occupations. At one end of the range it represents a direct transition from the defect level to the bottom of the conduction band; while at the other extreme,

in equilibrium it is for a transition from the defect level to the Fermi energy. Assuming minimum compensation, a reasonable estimate of E_F at non-zero temperatures below the ionization of residual donors is midway between the 18 meV level for the dominant donors and the bottom of the conduction band. Thus our $\sim$5 meV activation energy translates to a Mu[0/+] level somewhere between 5 and 14 meV below the conduction band edge. Considering the difficulty in interpreting the Mu ionization energy and ambiguity in determining the level of the shallower low-concentration donor in Ref. [8], the hydrogen equivalent of the observed Mu^0 center might be a candidate for this additional donor.

It is interesting that for Mu/H in GaN, no such shallow states are predicted in the latest theoretical studies [20, 21]. Our observation may not be incompatible with those predictions if the muon location that yields the shallow center were metastable rather than the lowest energy site. Of the two sites that locally satisfy the hyperfine symmetry, $\mathrm{BC}_{\parallel}$ is one of the lower-energy positions for both neutral and positive change states. Data for hydrogen at high temperatures [19] indicate that both the $\mathrm{AB}_{N\perp}$ and $\mathrm{BC}_{\parallel}$ sites are occupied during H^+ diffusion. The other likely site, $\mathrm{AB}_{N\parallel}$, is at a significantly higher energy, but yields a (meta)stable location for Mu^+ based on level-crossing results [13]. The same 'cage' region of the GaN structure that contains $\mathrm{AB}_{N\parallel}$ also contains the $\mathrm{AB}_{Ga\parallel}$ site found for a metastable Mu^-. A transition from Mu^+ to Mu^- at these sites, observed above 150 K, must involve a short-lived neutral that remains inside this cage. Related to the question of site, the origin for the high degree of anisotropy in the Mu hyperfine coupling is yet to be understood. A theoretical study of the shallow-donor N-H complex in diamond [22] may prove helpful on this issue.

More than 60% of implanted muons form diamagnetic states even at the lowest temperature. Our data indicate that whenever the shallow Mu^0 is present, the diamagnetic signal shows a fairly rapid exponential relaxation, characteristic of fast dynamics such as a transition out of that state. One possibility is that either Mu^+ or Mu^-, both of which were identified in the previous experiments [13], represents the initial state formed upon implantation and is a precursor to slightly delayed formation of the shallow neutral Mu center.

Further experiments, including *muonium* level crossing resonance measurements, are clearly required to clarify the detailed electronic structure and to more precisely identify the site of the observed shallow Mu^0 center.

In summary, we have demonstrated that a paramagnetic muonium center with extremely small hyperfine parameters is formed in GaN below 25 K. This Mu^0 center has a hyperfine interaction that is axially symmetric around [0001]. The temperature dependence of the yield for this state indicates that it acts as a shallow donor, strongly suggesting that hydrogen, if located at an equivalent crystallographic site, would contribute to the unintentional n-type conductivity in GaN.

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